

Tri(1-adamantyl)methane and its Thermolysis

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The synthesis of the title compound, a new tri(*tert*-alkyl)methane, and the kinetics and products of its thermolysis are described.

Tri(*tert*-butyl)methanol remained the unique tri(*tert*-alkyl)-methanol from 1945¹ until the synthesis of an analogue with one 1-adamantyl group in 1978,² then followed by many others.³ The corresponding methane⁴ was the sole tri(*tert*-alkyl)methane from 1970 to 1984 when a second was reported⁵ (both synthesised by reduction of the *p*-nitrobenzoates) but the series was not subsequently extended. We wish to report now the synthesis of tri(1-adamantyl)methane, **1**, by a method which opens up possibilities for further developments in this area.

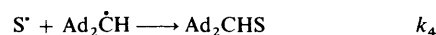
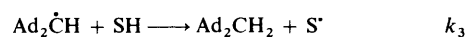
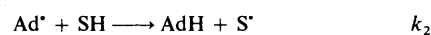
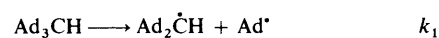
By treatment of tri(1-adamantyl)methanol with oxalyl halides in benzene at room temperature the corresponding methyl chloride⁶ and bromide⁷ have been prepared. The chloride was unreactive but reduction of the latter by tributyl tin hydride in refluxing benzene in the presence of AIBN gave methane **1** in 88% yield.*

The very low solubility of **1** makes NMR spectral study difficult but the ¹H spectrum in benzene shows broad signals associated with adamantyl groups and a sharp singlet at 1.40 ppm, close to that of the C–H proton in tri-*tert*-butylmethane⁴ (1.38 ppm in CCl₄). The ¹³C spectrum showed in particular a signal for the tertiary carbon at 66.9 ppm, as compared to values of 64.9 and 65.8 ppm for Bu^t₃CH and AdBu^t₂CH, respectively.⁵ The IR spectrum is very similar to that of Bu^t₃CH,⁴ with that of the deuterium-labelled compound (by Bu₃SnD) showing C–D absorptions at 2098 and 2122 cm⁻¹.

Thermolysis of **1** in toluene (SH) at 180–230 °C was clean and predictable (Table 1), apart from the formation of small amounts of di(1-adamantyl) ketone, Ad₂CO, and di(1-adamantyl)methanol, Ad₂CHOH (accounting together for about 8% of the initial hydrocarbon, and probably arising by reaction of the intermediate radical, Ad₂ĊH, with adventitious water in the solvent or on the glass tubes). The bibenzyl yield is almost equal to that of di(1-adamantyl)methane, Ad₂CH₂, as required by Scheme 1.†

* M.p. 277 °C (decomp.) (Found: C, 88.7; H, 10.8. C₃₁H₄₆ requires C, 88.92; H, 11.08%). $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 979, 1104, 1263, 1300, 1344, 1357, 1450, 2845, 2881, 2905, 2976, 3001, 3059; Ad₃CD also shows C–D stretching at 2098 and 2122 cm⁻¹. $\delta_{\text{H}}([\text{}^2\text{H}_8]\text{benzene}, 400 \text{ MHz}, \text{TMS})$ 1.40 (s, 1 H), 1.72 (q, 18 H), 2.00 (br s, 9 H), 2.33 (d, 18 H). δ_{C} 30.7 (CH of Ad), 37.7 (CH₂ of Ad), 43.8 (CH of Ad), 44.4 (CH₂ of Ad), 66.9 (CH).

† The Ad₂CH₂ peak was compared with an internal saturated hydrocarbon standard by GC and the first-order rate constant obtained by plotting $\log(R_{\infty} - R_t)$ against time, where R_{∞} and R_t are peak ratios (product/standard) at 'infinity' and time t . Duplicate runs gave rate constants agreeing to within about $\pm 3\%$. Product yields were determined by calibration against authentic samples at concentrations similar to those found in the thermolysis samples. 1,1-Di(1-adamantyl)-2-phenylethane, Ad₂CHS, was identified by its ITD spectrum: m/z (Finnigan MAT ITD 800B with chemical ionisation) 373 (11%; M⁺ – 1), 297 (7; M⁺ – C₆H₅), 239 (6), 238 (26; M⁺ – AdH), 237 (27), 136 (13, Ad⁺ + 1), 135 (100, Ad⁺). [²H₈]Ad₂CHS: m/z 380 (11%), 299 (6), 245 (10), 244 (32), 243 (16), 136 (13), 135 (100). For calibration, Ad₂CHS was replaced by Ad₂C=CHPh, obtained by thionyl chloride dehydration of 1,1-di(1-adamantyl)-2-phenylethanol.⁸ Ad₂CH₂, Ad₂CO, Ad₂CHOH and Ad₂CHS accounted for 97–98% of the intermediate di(1-adamantyl)methyl radical.



Scheme 1

Very small amounts (1–3%, increasing with the temperature) of a cross-product, identified by mass spectroscopy (Finnigan Ion Trap Detector) as 1,1-di(1-adamantyl)-2-phenylethane, Ad₂CHS (where S is PhCH₂), were found. The cross-product yield was much less than in the case of the corresponding alcohol⁸ (6–11% at 145–185 °C) or chloride⁹ (8–22% at 127–180 °C). This means that for di(1-adamantyl)methyl radical, Ad₂ĊH, the ratio of hydrogen abstraction from the solvent (k_3) to reaction with the solvent radical (k_4), is substantially higher than for Ad₂ĊOH or Ad₂ĊCl. Rate constant k_2 must be much greater than k_3 , since no 1-(1-adamantyl)-2-phenylethane AdS, is formed, even in [²H₈]toluene. The hydrogen isotope effect on k_3 , estimated by running the reaction in [²H₈]toluene (Ad₂CHS: 5–12%) and kinetic simulation⁸ of the Ad₂CHS/Ad₂CH₂ ratio (Table 2), was found to be somewhat less (decreasing regularly from 4.6 to 3.8 as the temperature increased) than the corresponding data for tri(1-adamantyl)-methanol thermolysis at lower temperatures (7.3–6.0 in the range 145–185 °C).¹⁰ Simulation indicated that, at the common temperature of 185 °C, Ad₂ĊH abstracts hydrogen from toluene about eight times faster than Ad₂ĊOH but three times slower than the *tert*-butyl radical. Comparison of the activation parameters reveals that the radical Ad₂ĊH lies between the *tert*-butyl and di(1-adamantyl)ketyl radicals,⁸ with the activation enthalpy and entropy for hydrogen abstraction from [¹H₈]toluene having values of 12.9 kcal mol⁻¹ and –20 cal mol⁻¹ K⁻¹, respectively.‡ Corresponding values for [²H₈]toluene are 15.0 kcal mol⁻¹ and –18.4 cal mol⁻¹ K⁻¹. The first-order decay of Ad₂ĊH in normal toluene in the range 180–240 K is reported⁷ to have an Arrhenius activation energy of 4.8 kcal mol⁻¹ and a pre-exponential factor of 6×10^3 , neither of which is in keeping with our results which give for the pseudo-first-order rate constants, $k_4[\text{tol}]$: $E_a = 13.0 \text{ kcal mol}^{-1}$ and $\log(A/s^{-1}) = 9.5$.

Activation parameters for the thermolysis of Ad₃CH are: $\Delta H^{\ddagger} = 45.2(\pm 0.2) \text{ kcal mol}^{-1}$ and $\Delta S^{\ddagger} = 17.8(\pm 0.4) \text{ cal mol}^{-1} \text{ K}^{-1}$, the activation entropy being typical for thermolysis of such systems.¹¹ In previous work¹² we obtained for the thermolysis of *tert*-butyldialkylmethanes,¹³ Bu^tR¹R²CH, an approximate relationship between the activation energy at 200 °C and the difference in the molecular mechanics (MM2 force field)¹⁴

‡ 1 cal = 4.184 J.

Table 1 Temperature and solvent isotope effects on product composition (%) from the thermolysis of tri(1-adamantyl)methane in toluene

T/°C	Yields					
	Bibenzyl	Ad ₂ CH ₂	Ad ₂ CO	Ad ₂ CHOH	Ad ₂ CH ₃	Total Ad ₂ ĊH
In [¹ H ₈]toluene ^a						
185	89.2 (98.7)	89.6 (98.8)	3.7	3.8	1.1 (1.2)	98.2
200	88.5 (100.5)	88.3 (98.2)	3.7	3.4	1.6 (1.8)	97.0
214.5	88.0 (99.2)	88.2 (97.55)	3.6	3.2	2.2 (2.45)	97.2
230	88.7 (101.0)	87.3 (96.5)	3.9	3.3	3.2 (3.5)	97.7
In [² H ₈]toluene ^b						
185	87.2 (93.6)	88.2 (94.6)	4.7	2.2	4.9 (5.4)	
200	85.7 (91.6)	86.7 (92.65)	4.1	2.6	6.7 (7.35)	
214.5	84.5 (91.1)	84.2 (90.75)	4.3	3.2	8.3 (9.25)	
230	81.4 (87.4)	81.9 (87.95)	4.4	2.8	10.9 (12.05)	

^a Absolute yields; normalised values in parentheses. ^b Relative yields; normalised values in parentheses.

Table 2 Kinetic simulation of product data for thermolysis of tri(1-adamantyl)methane in toluene (assumed $k_4 = k_5$; $k_2 \gg k_6$)

T/°C	[Ad ₃ CH] ₀ / mol dm ⁻³	[tol]/ mol dm ⁻³	k_1/s^{-1}	$k_5/10^{11}$ dm ³ mol ⁻¹ s ⁻¹	k_3 [tol]/ 10 ³ s ⁻¹	$k_3/10^2$ dm ³ mol ⁻¹ s ⁻¹	(ΔG^\ddagger) ₃ / kcal mol ⁻¹
In [¹ H ₈]toluene							
185	0.001 67	7.55	0.610×10^{-4}	0.152	2.16	2.86	22.06
200	0.001 62	7.34	0.302×10^{-3}	0.169	3.32	4.53	22.39
214.5	0.001 57	7.12	0.129×10^{-2}	0.186	5.07	7.12	22.66
230	0.001 52	6.90	0.600×10^{-2}	0.204	7.67	11.1	22.97
In [² H ₈]toluene							
185	0.001 86	7.55	0.610×10^{-4}	0.152	0.467	0.618	23.46
200	0.001 81	7.34	0.302×10^{-3}	0.169	0.767	1.05	23.76
214.5	0.001 75	7.12	0.129×10^{-2}	0.186	1.25	1.76	24.01
230	0.001 70	6.90	0.600×10^{-2}	0.204	2.04	2.96	24.29

strain energies of the initial hydrocarbon and R¹R²CH₂, taken as a transition state surrogate.

$$\Delta G^\ddagger = 75.3(\pm 1.7) - 1.08(\pm 0.08)\Delta \text{ strain}$$

In the present case allowance has to be made for the fact that the Ad[•] radical formed has non-zero strain energy: 10.4 + 2.4 kcal mol⁻¹, the first term being the MM2 strain energy of adamantane and the second the relative difference between the strain energies of the Ad[•] and Bu[•] radicals.¹¹ With the strain energies of Ad₃CH and Ad₂CH₂ calculated as 76.0 and 28.3 kcal mol⁻¹, respectively, one predicts $\Delta G^\ddagger = 37.7$ kcal mol⁻¹, which is in good agreement with the experimental value of 36.8 kcal mol⁻¹.

MM2 (or MM3)¹⁵ calculations indicate that **1** is geometrically similar to Bu^t₃CH whose structure is known from an electron diffraction study¹⁶ and has been calculated more or less well with various force fields.¹⁷ Both molecules are rather flat, with the H-C_i-C_q bond angle about 100° and C_q-C_i-C_q about 116°; the C_i-C_q bonds in **1** should be slightly longer (1.63 Å) than in Bu^t₃CH (1.61 Å), but the involatility of tri(1-adamantyl)methane, and the difficulty of obtaining crystals, for the moment preclude experimental investigation.

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